A FEASIBILITY STUDY OF THE APPLICATION OF SOLVENT EXTRACTION AND GAS LIQUID PARTITION CHROMATOGRAPHY TO MARINE TRACE-METAL ANALYSIS

A

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A FEASIBILITY STUDY OF THE APPLICATION OF SOLVENT EXTRACTION AND GAS LIQUID PARTITION CHROMATOGRAPHY TO MARINE TRACE-METAL ANALYSIS

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ABSTRACT

This work is predominantly concerned with the extraction of Co, Fe, In, and Zn from a seawater matrix, using organic ligands and solvents selected on the basis of their suitability for trace analysis of these metals by gas liquid partition chromatography with electron-capture detection. The long-term aim of this work is an evaluation of the suitability of utilizing this method of analysis for trace metals present in seawater and other natural waters. High extraction efficiencies have been determined for all four metals. Thus 90% of added Co and 81% Zn may be extracted from seawater within one minute with toluene-trifluoroacetylacetone (0.1M)- isobutylamine (0.4M) over a wide pH range and a phase ratio of 10. 90% of an In spike is removed from seawater by toluene-trifluoroacetylacetone (0.1M) within five minutes over the pH range 6-10 with a 1:20 phase ratio. With a 1:40 ratio of this latter organic phase to seawater, 88.5% of added Fe is extracted within 10 minutes over a 4-10 pH range. This study has not determined suitable conditions for the chromatographic analysis of the Co, Fe, In and Zn-trifluoroacetylacetone chelaters. However, trace Al spikes were extracted from natural water samples using toluene-trifluoroacetylacetone (0.1M) and analysed by these procedures. The detection limit for natural waters is 6×10^{-12} g, under un-optimized extraction conditions.

ACKNOWLEDGEMENTS

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INTRODUCTION

In the past few years, marine trace element analysis has received much attention and has enjoyed significant success through the improvement of analysis techniques and the development of sensitive instrumentation. These achievements offer inorganic and physical chemists a step toward understanding the precise chemical composition of seawater and elucidation of the thermodynamic properties of the various chemical species present. Neutron activation analysis, atomic absorption spectrophotometry, and anodic stripping voltammetric analysis are the most commonly employed methods of analysis in this field.

Solvent Extraction Study

Solvent extraction, combined with gas liquid partition chromatography has been applied successfully to those metal ions which form coordination saturated chelates with trifluoroacetylacetone, where the coordination number of the metal ions does not exceed twice the central ion's charge and the metal ion is completely screened by the ligands only. But this is not the case for unsaturated chelates where the coordination number of their central ion is more than twice that of the metal charge. These unsaturated chelates retain free coordination positions, which, in general, are occupied by oxygen-containing ions or molecules. A chelate with coordinated water is dissolved poorly in non-oxygen-containing solvents of low polarity. To obtain a high solubility, it is necessary to displace the water molecules with molecules of some organic substance. Adduct formation usually will satisfy this requirement (Alimasin and Zolotov 1962).

For the extraction of the chelates formed by a given reagent with various elements, as a rule those solvents are used in which the reagent

itself and the chelates formed are readily soluble. Nevertheless, consideration of the solubility of a reagent and its chelate in the organic solvent is insufficient for this study. The needs of the electron-capture detector must also be considered. In general, the electron absorption conferred upon a compound is caused by the presence of an electrophore such as halogens, -OH, -CO, $-NO_2$, - NH_2, etc. on the molecule. A high quantity of such absorbing compounds present eventually causes this detector to respond strongly, so that interference problems are caused where a small quantity of strongly absorbing sample is present in a matrix of low absorbing compounds (Lovelock 1963). For example, ketones, esters, and especially alcohols can quantitatively extract both coordinated saturated and unsaturated chelates (Alimasin and Zolotov 1962), but these solvents are not suitable here simply because of their electron affinities. Toluene, therefore, has been employed as the principle solvent in this study. It has no electron affinity and has been previously used successfully for glpc studies (Moshier and Sievers 1965).

Elements which react with trifluoroacetylacetone to form chelates which have promise from the analytical point of view are listed in Table I. Metal ions of interest in this study are Al, In, Fe, Co and Zn, and their abundances in sea water are 0.01 ppm, < 0.02 ppm, 0.01 ppm, 0.0001 ppm and 0.01 ppm, respectively (Goldberg 1965).

Gas Liquid Partition Chromatography

Gas liquid partition chromatography (glpc), since its development, has been used primarily in organic chemistry and biochemistry. With the advent of the electron-capture detector (e.c. detector) - a detector specifically designed for measurements of compounds having an affinity

for free electrons and extremely sensitive to fluorine-containing chelates (Moshier and Sievers 1965) - its application to trace metal analysis has proved feasible in recent years: e.g., Cr in ferrous alloys (Ross and Sievers 1969), in blood and plasma (Hansen, Saibner, Gilbert and Sievers 1971), and in biological materials (Booth and Darby 1971); Al in uranium (Genty, Houin and Scott 1968); Al and Cr in uranium (Genty, Houin, Malherbe and Scott 1971); and Be in aqueous solution (Ross and Sievers 1968), and in biological specimens (Taylor and Arnild 1971). However up to the present time, there are no reports of the application of glpc to trace metal analysis in natural waters. Its application to metal analysis is still in its infancy. However, a rapid development in metal chelate analysis by glpc with an e.c. detector has occurred. One merit of this technique is its applicability to the trivalent metals, especially Al, which are less amenable to determination by other techniques.

A major problem in analyzing metals with gas chromatography has been the lack of volatility and the high reactivity of these compounds. In almost all cases, the metal compounds to be chromatographed must have a vapor pressure of the order of 0.1 to 1 mm to allow gas phase migration through the column at a reasonable rate. This means the compounds must be very volatile, and should be thermally and solvolytically stable.

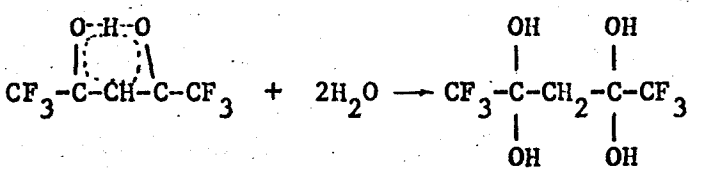
Metal-acetylacetone (AcAc) chelates and their fluorinated derivatives were considered to be primary candidates for the study.

AcAc readily reacts with the active metals such as the alkali and alkaline earth elements which are the most abundant elements found in seawater. So AcAc may be cancelled from the candidate list. Quite a

few studies reveal that the fluorinated AcAc chelates are more volatile and thus can be eluted at lower column temperature than acetylacetonates (Moshier and Sievers 1965). Chelates of trifluoroacetylacetone (tfa) can be eluted at column temperatures between 100 and 150°C. Chelates of higher fluorinated AcAc allow even lower column temperature (Moshier and Sievers 1965).

Chelates of fluorinated AcAc attract attention not only because of their volatilities and selectivities but also because the fluorine atoms present have high electron electronegativity and therefore make the detection of ultratrace quantities by e.c. detector feasible. Among fluorinated acetylacetonates, the most thoroughly studied chelates are those of trifluoroacetylacetone (tfa) and hexafluoroacetylacetone (hfa).

The vapor pressure and the relative ease of elution of the AcAc derivatives are proportional to the degree of fluorination. It would seem that hfa is a better chelating agent. But, hfa tends to react with water to give 1,1,1,5,5,5-hexafluoro-2,2,4,4-tetra-hydroxypentane (Moshier and Sievers 1965):



For these reasons, tfa has been selected as the chelating agent for this work.

This study evaluates the conditions for solvent extraction of indium, iron, cobalt, zinc, and aluminum-tfa chelates from seawater into toluene and for chromatographic analysis of these chelates.

EXPERIMENTAL

A. Solvent Extraction

Reagents.

All reagents used were Baker reagent grade unless otherwise specified. Isobutylamine (iba) and trifluoroacetylacetone (1,1,1-trifluoropentane-2,4-dione) were obtained from Columbia Organic Chemicals Company. This compound was distilled and the fraction boiling from 106 to 107° C was collected and stored at 5° C. The indium powder came from ALFA Inorganic Company. Toluene and benzene were Mallinckrodt nanograde, and all liquid phases and the Gas Chromo Z solid support were obtained from Applied Science Company.

Preparation of chelates

Reagents.

$CuSO_4$, $Fe(SO_4)_3$, $Al(NO_3)_3$, sodium acetate, absolute ethyl alcohol, and $InCl_3$, synthesized by dissolving powdered indium in the minimum amount of redistilled HCl.

In, Fe, and Cu chelates:

25 g metal compound and 15 g sodium acetate were dissolved in 250 ml double distilled water. The solution was then mixed with 200 ml ethanol-tfa (0.1M) solution and the mixture was shaken for 40 minutes; though reaction begin in minutes. The precipitate was recrystallized with Baker G.C. - grade benzene.

Al chelate:

Since $Al(NO_3)_3$ contained a trace amount of impurity, the precipitate

was yellow in color. This chelate cannot be purified with repeated hexane or benzene extraction. Since Fe and Cu chelates are formed within minutes, a simple method for Al-tfa preparation was developed: 250 ml 0.1M tfa solution to Al solution were mixed with sodium acetate, the mixture shaken for 20 minutes, the precipitate discharged, and the supernatant shaken until reaction was complete. The precipitate was recrystallized with benzene and dried under vacuum at room temperature. Pure white Al-chelate was thus obtained.

The melting points of the synthesized chelates were measured with a Fisher-Johns melting point apparatus. The melting point of Cu-tfa was 199.5±0.5°C, Fe-tfa was 114°C, Al-tfa 122°C, and, In-tfa 123.5°C (Table I).

Extraction procedure (Table II):

A seawater sample (pH 7.84) was adjusted to various pH subsamples with NaOH and HCl. 15-ml aliquots of each subsample were added to 125-ml separatory funnels with teflon stopcocks, and treated with 2-ml of In^{114m}, Fe^{59}, Co^{60}, or Zn^{65} solution. The labelled seawater was then mixed well and 2-ml aliquots were taken for radioactive counting. 15-ml of reagent solution, toluene-tfa(0.1M) or toluene-tfa(0.1M)-isobutylamine(0.4M) were added to the funnel and the mixture was mechanically shaken for ten minutes (60 minutes for indium). After equilibrium, the mixture was allowed to stand until the two phases separated. 2-ml aliquots of each phase were taken for counting. The pH of the aqueous phase was taken to be the equilibrium pH. Since pH is defined operationally in terms of a cell and the measurement is made by comparing the solution with a standard buffer, it is assumed $pH \simeq p\,a_H \simeq -\log(H^+)$. Various amounts of seawater, and different

equilibrium times were also used for checking the extraction efficiency as a function of water/organic phase ratio and the equilibrium time. The affect of the concentration of isobutylamine (iba) on the extraction of Zn was also studied.

Radioactive counting

For gamma counting, 2-ml of the initially labelled aqueous phase, and the equilibrated aqueous and organic phase were pipetted into a test tube. The energy window of a Picker dual channel scintillation counter was adjusted for different tracers and the samples were counted for a time period of up to 10 minutes in order to minimize statistical counting errors. The number of counts of each sample was subtracted from that of the background counts. Only one measurement was made for each element. Negative values (See Tables) mean the sample counts are lower than the background counts.

The values of the percent extraction of the metal ions were calculated by dividing the counts of the equilibrated aqueous phase by those of the initial aqueous phase.

The percent deviation of the counting is 2.4, calculated from a standard deviation of 32 background counts.

Interference of magnesium on zinc extraction

Because magnesium is a divalent-metal and its abundance in seawater is so high compared with that of zinc and cobalt, it was considered that it might interefere with the extraction of the latter two ions. It was also believed that the interference of Mg on Zn extraction might serve as an indicator of potential intereferences of Mg on Co extraction, and

also the possible effect of Ca, Sr, etc. ions on the extraction of Zn and Co. Here the interference of Mg on Zn extraction only was studied. An aqueous sodium chloride solution with the Na concentration similar to that of seawater was divided into two subsamples. To one subsample was added enough $MgCl_2$ to make a concentration of Mg equaling that in seawater. The subsequent extraction procedure was carried out as described above after Zn^{65} was added.

B. Gas Liquid Partition Chromatography

Apparatus.

A Varian Model 1520B gas chromatograph equipped with a tritium e.c. detector (and a model A-25 recorder) was used for this investigation. A Varian voltage regulator (Model 630) was employed for reducing cell voltage. The injection port of the gas chromatograph was modified for on-column injections. The injector insert was removed and the end of a 6mm o.d. glass column was inserted into the injector to within 7.mm of the septum. A 10µl syringe was used for sample injection. The needle was long enough to inject sample into the column at least 15mm (Fig. 1).

Six 150mm x 6mm o.d. pyrex glass columns were each packed with a single liquid phase or a mixture on 60-80 mesh Gas Chromo Z. Columns packed were the following: 4% polyethylene 600, 13% carbowax 20M, 6% carbowax 20M - 10% apiezon L, 5.08% silicone SE30 - 0.34% carbowax 20M, and 4.6% DC710 - 0.2% carbowax 20M.

Column Preparation

Choice of liquid phase:

The correct choice of a liquid phase is one of the important parameters in glpc. Notably the partitioning solvent chosen should have the following characteristics:

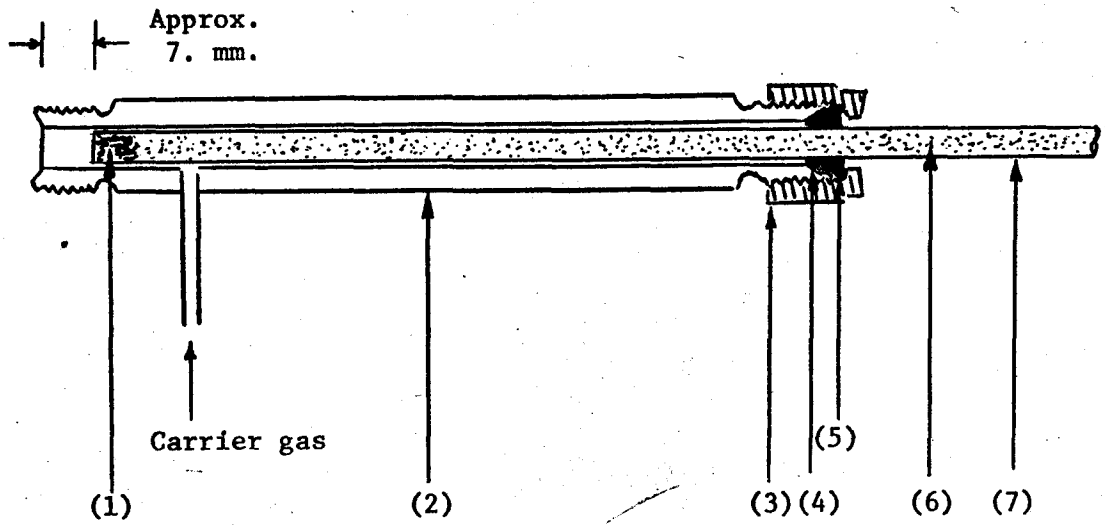


Fig. 1 Column installation in injection port for on column injection.

(1) Glass wool.

(2) Injector.

(3) Swagelok nut.

(4) Teflon front ferrule.

(5) Teflon back ferrule.

(6) Coated support.

(7) Glass column.

1. Samples must exhibit different distribution coefficients.

2. The liquid phase should have a negligible vapor pressure at operating temperature.

3. The liquid phase should be chemically inert and thermally stable at the operation temperature.

4. The liquid phase should be similar in chemical structure to the components of the mixture.

Different polarity liquid phases, polyethylene glycol 600, carbowax 20M, Silicone 710, were chosen to separate mixtures by interaction forces. Non-polar liquid phases, Apiezon L, and Silicone SE30 were employed for the metal-chelates of different boiling points (Table III). Final choice of liquid phase was based on the resolution of chelates and solvent peaks.

Coating Support:

The support was coated by the method suggested by Parcher and Urone (1964). An excess amount of liquid phase solution was placed in the coating chamber and the solid support was then poured into the solution and mixed well. The solution was drained off with slight suction. The support was dried with slight heating and a stream of warm nitrogen gas. After the particles were uniformly dried, the flow of the gas was adjusted to blow off the fine particles and fragments. A small amount of coated support was weighed and washed with solvent to remove the liquid phase coating. Percent coating was calculated by dividing the dry weight of the support by its original weight. This technique has the advantages of saving time and the support is evenly coated and of a more homogeneous size.

Conditioning the Column:

All the columns were pre-conditioned for 24 hours at 25°C below the lowest recommended maximum temperature of the liquid phases.

Determination of GC operating conditions

With cell voltage set at 20V and all other instrument conditions constant, the flow rate was varied and the observed peak height vs. flow rate plotted (Figs. 8 and 9). Then with the nitrogen flow rate set at 114 ml/min and all other instrument conditions static, the cell voltage was varied by 5-volt increments from 5 to 90. The peak height vs. applied voltage was plotted (Figs. 10 and 11) and the highest response was considered the optimum applied potential. The detector response to the applied voltages (10V, 15V, and 20V) at flow rate 285 ml/min was also determined (Fig. 11).

Optimum gas chromatography operating conditions.

Injection port: On-column injection at 122°C.

Column temperature: 118°C.

Applied voltage: 5V.

Detector temperature: 205°C.

Carrier gas: Prepurified nitrogen.

Flow rate: 285 ml/min.

Column: 150mm x 6mm o.d. glass column, packed with 4.6% DC 710 and 0.2% carbowax 20M on 60-80 mesh Gas Chromo Z.

Electron-capture detector cleaning procedure.

The procedure was a modification of the method of Holden and Wheatley (1967). The tritium foil and detector cell were boiled in 5 ml 5% alcoholic KOH solution for three minutes and wiped with tissue

while in the solution. Then both were boiled for another minute in 50 ml of the solution. The foil and cell were cleaned in hot double distilled H_2O, rinsed with hot water twice, and with hot alcohol thrice. Finally, the tritium foil and detector cell were air-dried for 15 minutes.

Sample preparation for chromatography

The following procedure was used for analysis of the chelate by electron-capture gas liquid partition chromatography. 30 ml of seawater were introduced into a separatory funnel. 15 ml of 0.1M tfa solution were added, and the mixture was shaken for one hour. The aqueous phase was then decanted. Since the quantities of metal extracted were very small, only a minute amount of tfa was consumed in the extraction and the excess of tfa was then dissolved with the metal-tfa in the organic phase. Because tfa is a high electron affinity molecule, it causes a strong detector response. Removal of unreacted tfa from the organic phase was accomplished by the NH_4OH wash suggested by Genty et al. (1968), but for the sake of time, the organic phase was washed for 10 seconds twice instead of 15 minutes once with 20-ml of 0.01 N NH_4OH solution. A 2.0 µl sample was taken for chromatographic injection using a Hamilton microsyringe.

In a further study of the extractability of Al from seawater, a known amount of Al(10^{-6} g) as nitrate was added to 30-ml of seawater and extracted and chromatographyed as described above.

To pursue the possibility of utilizing these proposed techniques for the determination of the metal ions in fresh water, some lake water samples were collected and prepared for chromatographic analysis. The water of Smith Lake, College, Alaska, has a high organic content, which caused the e.c. detector to function abnormally. Therefore, the organic matter was decomposed with UV light before the extraction procedure given was carried out.

RESULTS

A. Solvent Extraction

Indium. Indium was rapidly 99.5% extracted over the pH range 6.3 to 10 with phase ratio 1:1 (Fig. 2 and Table IV) in a single extraction within five minutes (Fig. 3 and Table V), and 90% of the indium present can be removed with an aqueous/organic volume ratio of 20 (Fig. 4 and Table VI).

Iron. Over the pH range 4-10, iron was effectively removed (Fig. 2 and Table VII) with equal volume of reagent solution and equilibrium was reached within 10 minutes (Fig. 3 and Table VIII). With a phase ratio of 40, an 88.5% extraction was obtained (Fig. 4 and Table IX).

Zinc. No zinc or only a trace of zinc was extracted from seawater at any pH (Fig. 2 and Table X) using equal volume of toluene-tfa (0.1M). This inability was apparently not due to the presence of the major divalent ions (i.e., magnesium; Table XI). Zinc was instantaneously and quantitatively extracted, however, from seawater over the pH range studied with the organic solvent pair toluene-tfa(0.1M)-isobutylamine (0.4M) (Figs. 5 and 6, and Tables XII and XIII). Lesser extraction efficiencies of zinc were recorded whenever a trace of white precipitate was observed at the interface of the two phases (Fig. 5). Foams existed at the interface of all samples, but the extraction efficiency was not affected with volume ratio up to 50. Low extractability occurred if the aqueous/organic volume ratio was greater than 10 (Fig. 7, Table XIV); presumably the amount of isobutylamine added was insufficient. The organic phase was completely foamy if the phase ratio exceeded 50. The extraction of Zn was independent of extraction time.

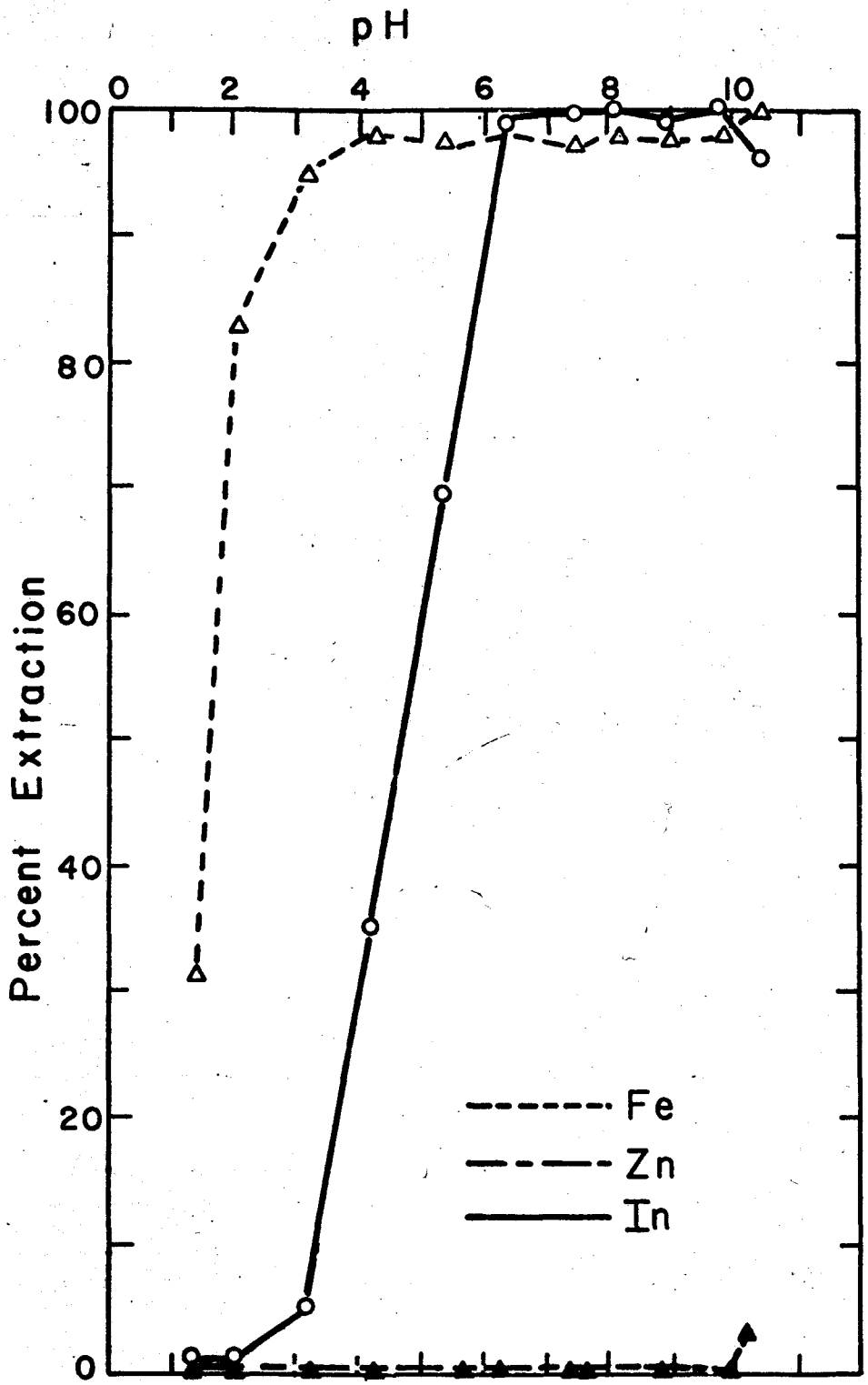


Fig. 2 **Effect of pH on extractability of iron, indium, and zinc from seawater with toluene-trifluoroacetylacetone (0.1M), phase ratio 1:1.**

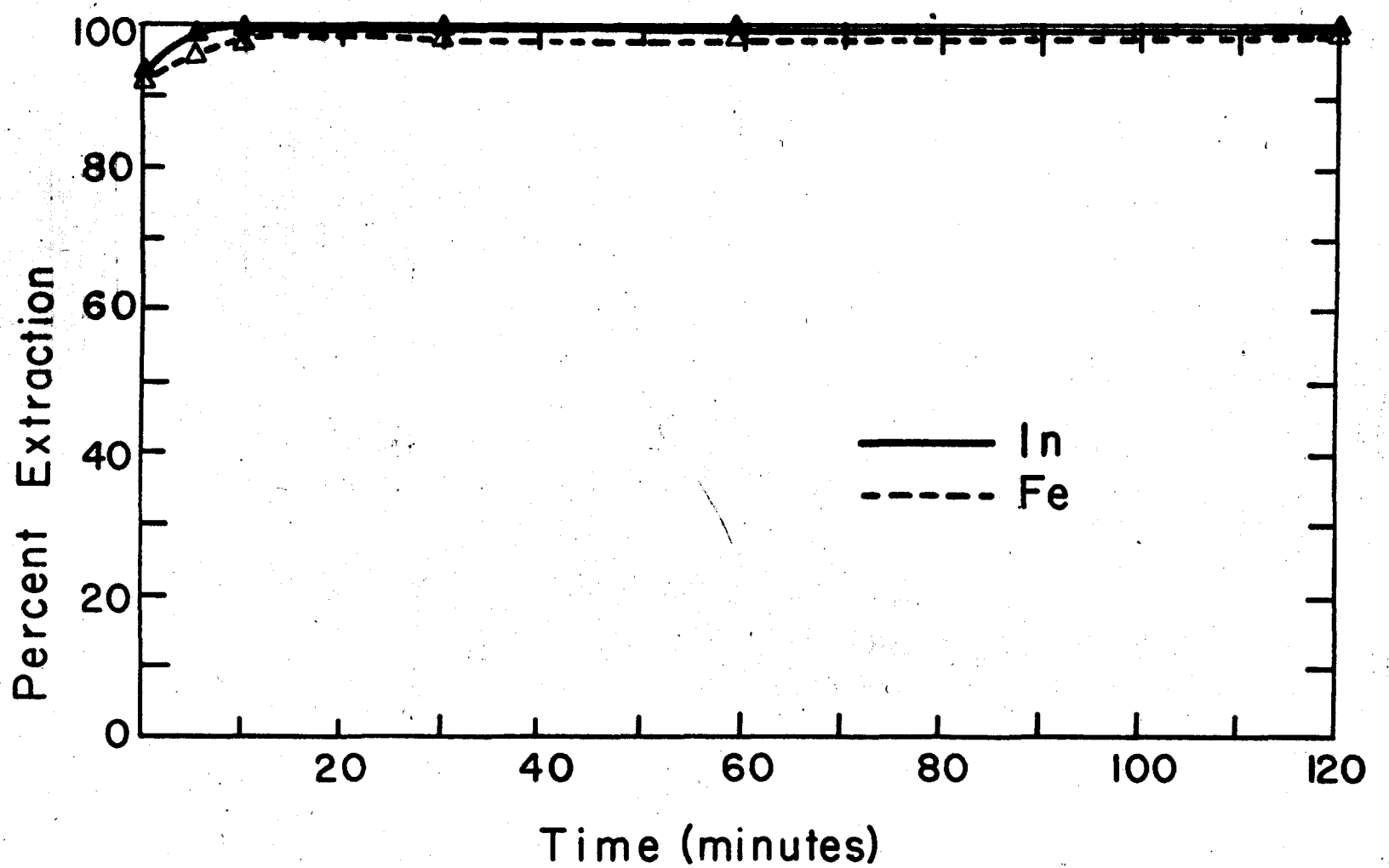


Fig. 3. Effect of time on extraction of iron and indium from seawater with toluene-trifluoroacetylacetone (0.1M), phase ratio 1:1.

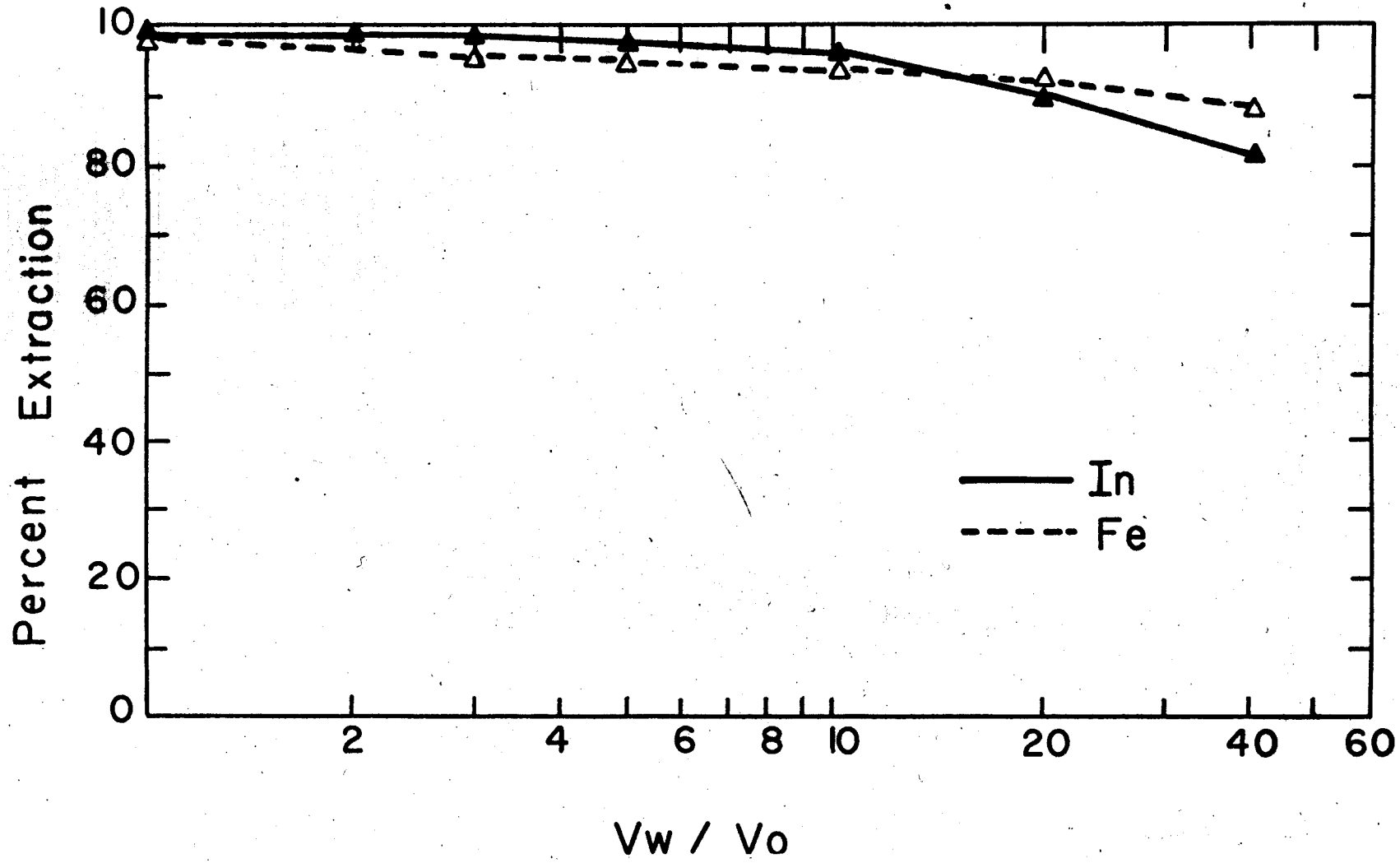


Fig. 4. Efficiency of extraction of iron and indium from seawater with toluene-trifluoroacetylacetone (0.1M) as a function of water/organic phase ratio.

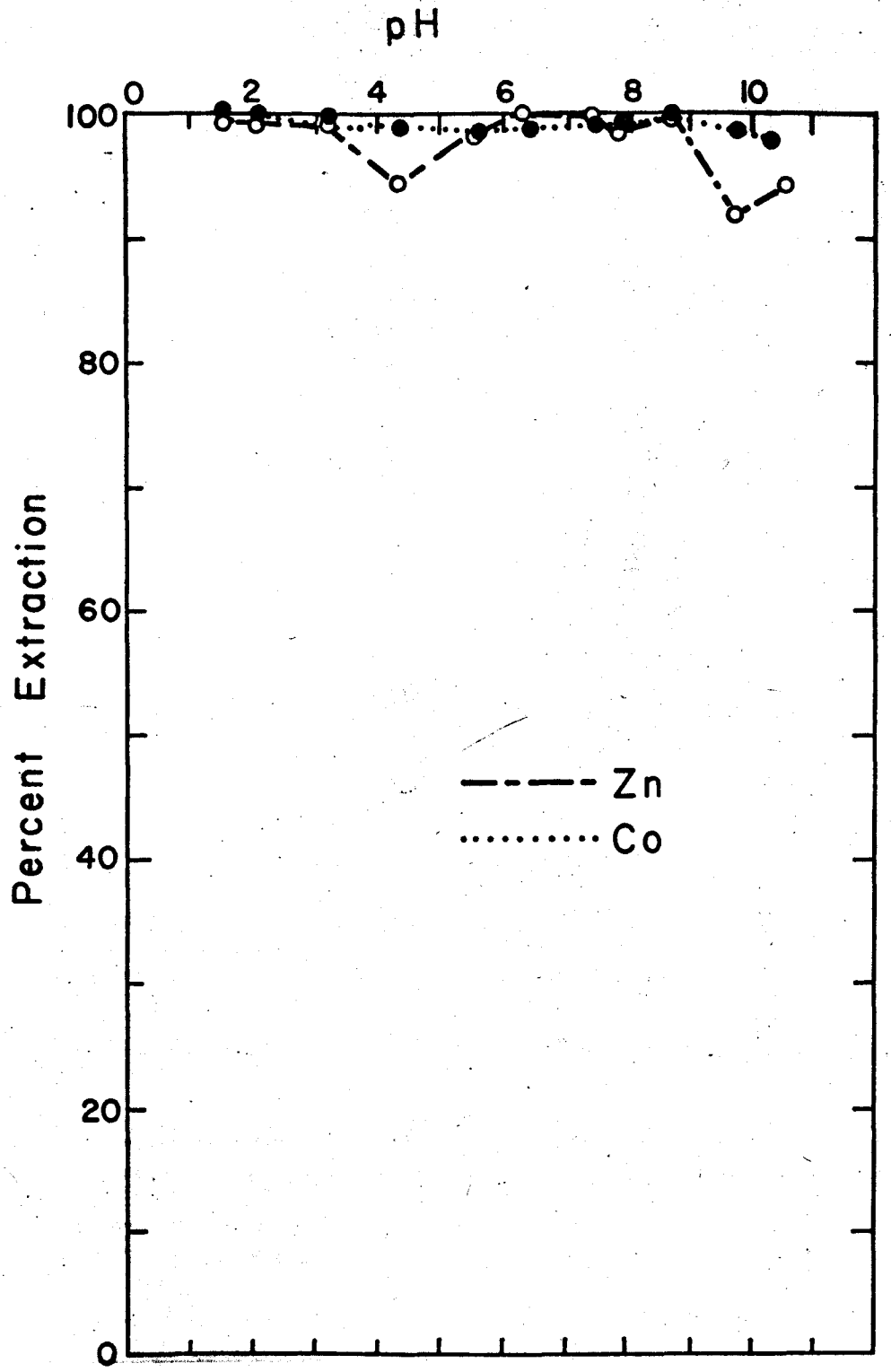


Fig. 5. Effect of pH on extractability of zinc and cobalt from sea water with toluene-trifluoroacetylacetone (0.1M)- isobutylamine (0.4M), phase ratio 1:1.

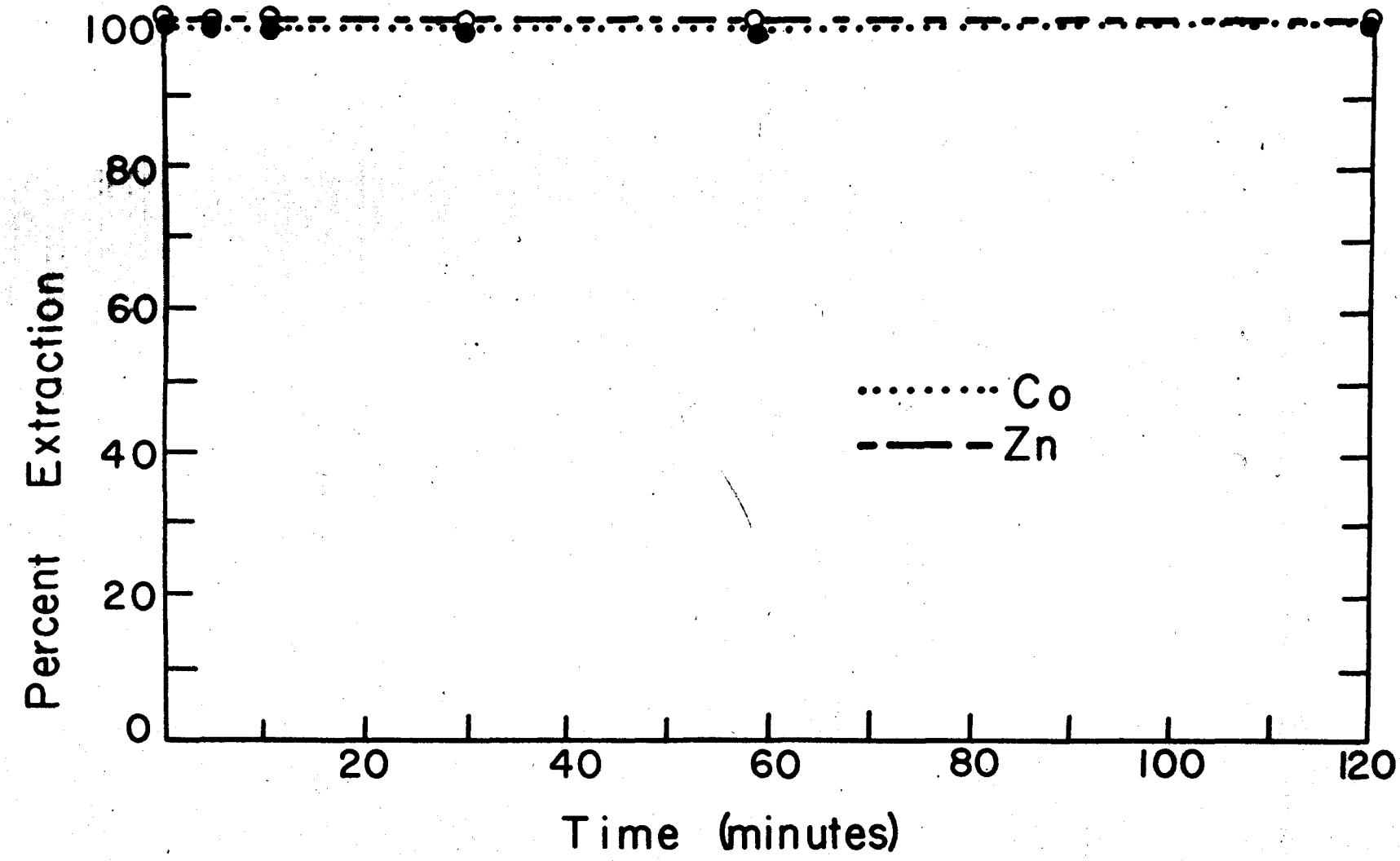


Fig. 6. Effect of time on extraction of cobalt and zinc from seawater with toluene-trifluoroacetylacetone (0.1M)- isobutylamine (0.4M), phase ratio 1:1.

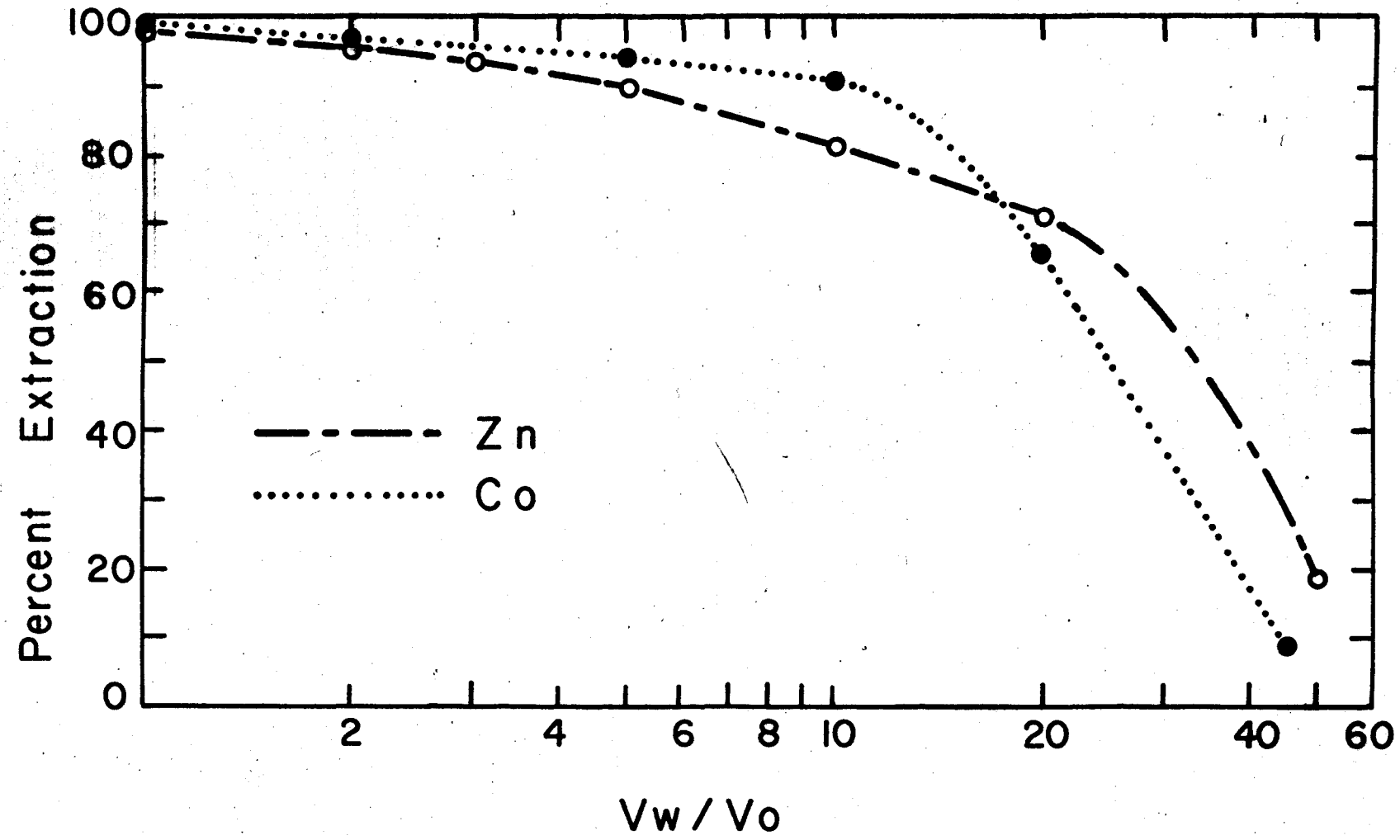


Fig. 7. Efficiency of extraction of zinc and cobalt from seawater as a function of water/organic phase ratio.

Cobalt(II). This is the dominant form of the dissolved Co species in seawater (Kranskopf 1956 and Fukai 1968). It was found that this ion also could not be extracted with toluene-tfa(0.1M) from seawater, but Co(II) was rapidly and completely removed from seawater with toluene-tfa(0.1M)-iba (0.4M) (Figs. 5 and 6, Tables XV and XVI). Precipitates and foams were observed at the interface but these did not interfere with the extraction. As the phase ratio exceeded 10, the percent of Co extracted decreased rapidly. As with Zn, the organic phase was completely foamy if the phase ratio exceeded 50 (Fig. 7 and Table XVII). The distribution of Co was independent of pH and extraction time over the range studied.

The amounts of isobutylamine added to the system was found to be very critical in the extraction of Zn and Co. For a 15 ml seawater sample, for example, at least 0.2 ml of isobutylamine is needed for 15 ml toluene-tfa (0.1M) solution (Fig. 8 and Table XVIII).

B. Gas Liquid Partition Chromatography

Liquid Phase

Polyethylene glycol 600 was not a suitable liquid phase for metal-tfa analysis, since high amounts of bleeding were observed at a column temperature of 110°C. The bleeding caused the e.c. detector background current to continuously drift. Carbowax 20M gave good resolution of chelate peaks but long tailing of the tfa peak overlapping the peak of Al-tfa. The loss of chelates by adsorption in this column was much less than with any of the other four columns, because the polar liquid phase saturated the active sites of the support. It was therefore decided to use mixed liquid phases with other columns. Columns made of 5.08%

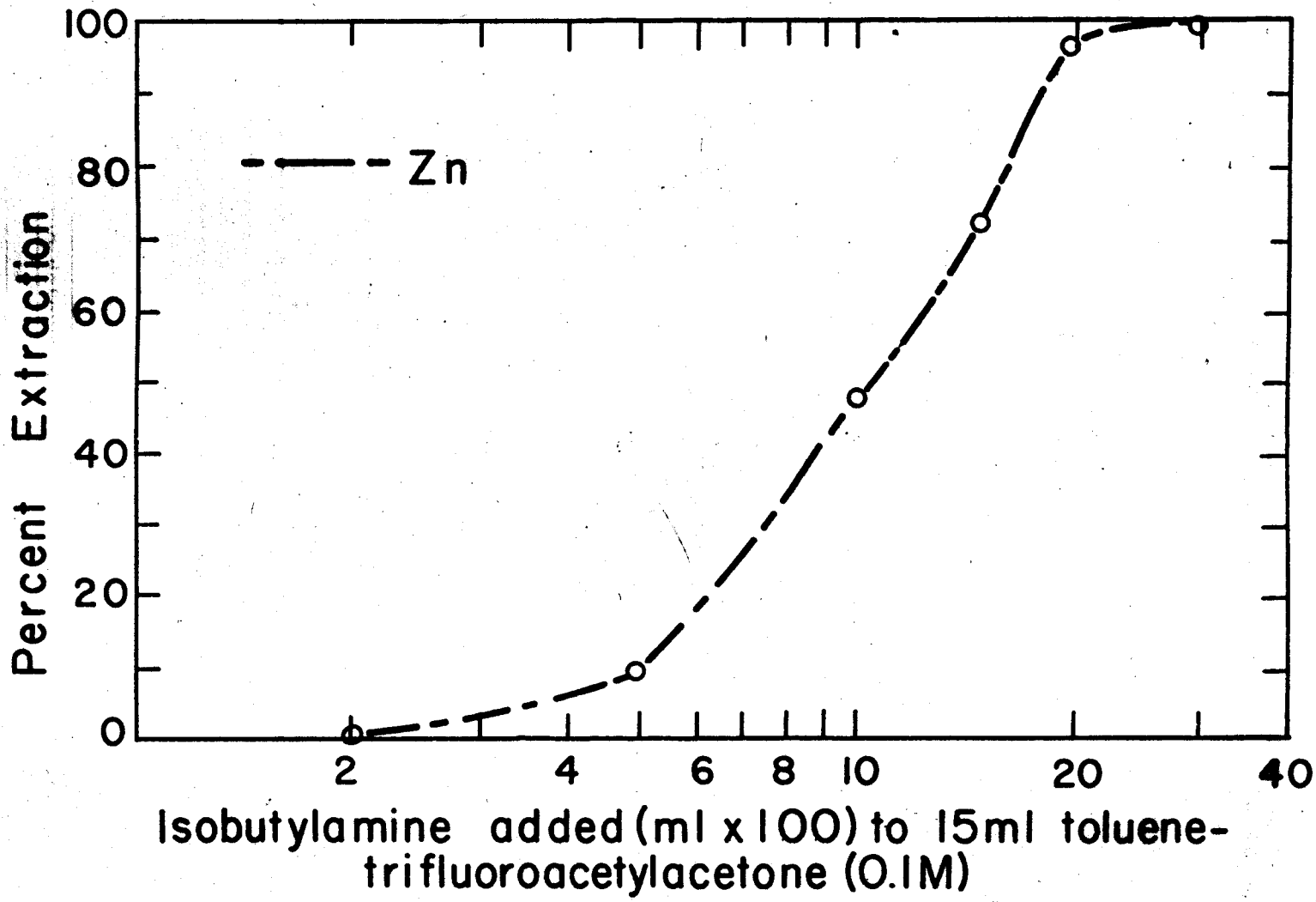


Fig. 8. Effect of the concentration of isobutylamine on the extractability of zinc from sea water with 15ml of toluene-trifluoroacetylacetone (0.1M), phase ratio 1:1.

silicone SE 30 and 0.34% carbowax 20M gave a good symmetric Al-tfa peak, excellent resolution of the peaks of Al-tfa and tfa, and a short retention time if the column length and diameter were appr[illegible] Adsorption problems were most serious in the column of 6% carbowax [illegible] and 10% apiezon L; the column gave good resolution of peaks but very long retention time.

On-column injection

The injection port temperature for flash vaporization injection is usually at least 20-30°C higher than the column temperature (Moshier and Sievers, 1965; Morie and Sweet 1966). This extra temperature probably causes the decomposition of iron and zinc chelates (Moshier and Sievers 1965). Many tfa chelates are eluted at column temperatures between 100 and 150°C, and an injection temperature of 135°C is necessary in order to get sharp peaks. However, this temperature will cause Fe-tfa, Mn(III)-tfa, Zr-tfa, Hf-tfa and Zn-tfa to decompose (Moshier and Sievers 1965). Reducing the injector temperature yielded a flattened peak. On-column injection employed in this study has solved both problems; the injector temperature is reduced, and the peak shape is maintained.

Optimum conditions for the electron capture detector

There are many operating parameters which affect the response of an e.c. detector to Al-tfa. The effects of flow rate and applied potential were studied. The sensitivity increased with increasing flow rate up to 285 ml/min (Figs. 9, 10 and 11; Table XIX); further increases in the flow rate intensified the detector response, but with a highly unstable background signal. Increasing the cell voltage decreased sensitivity tremendously (Figs. 11 and 12, Table XX).

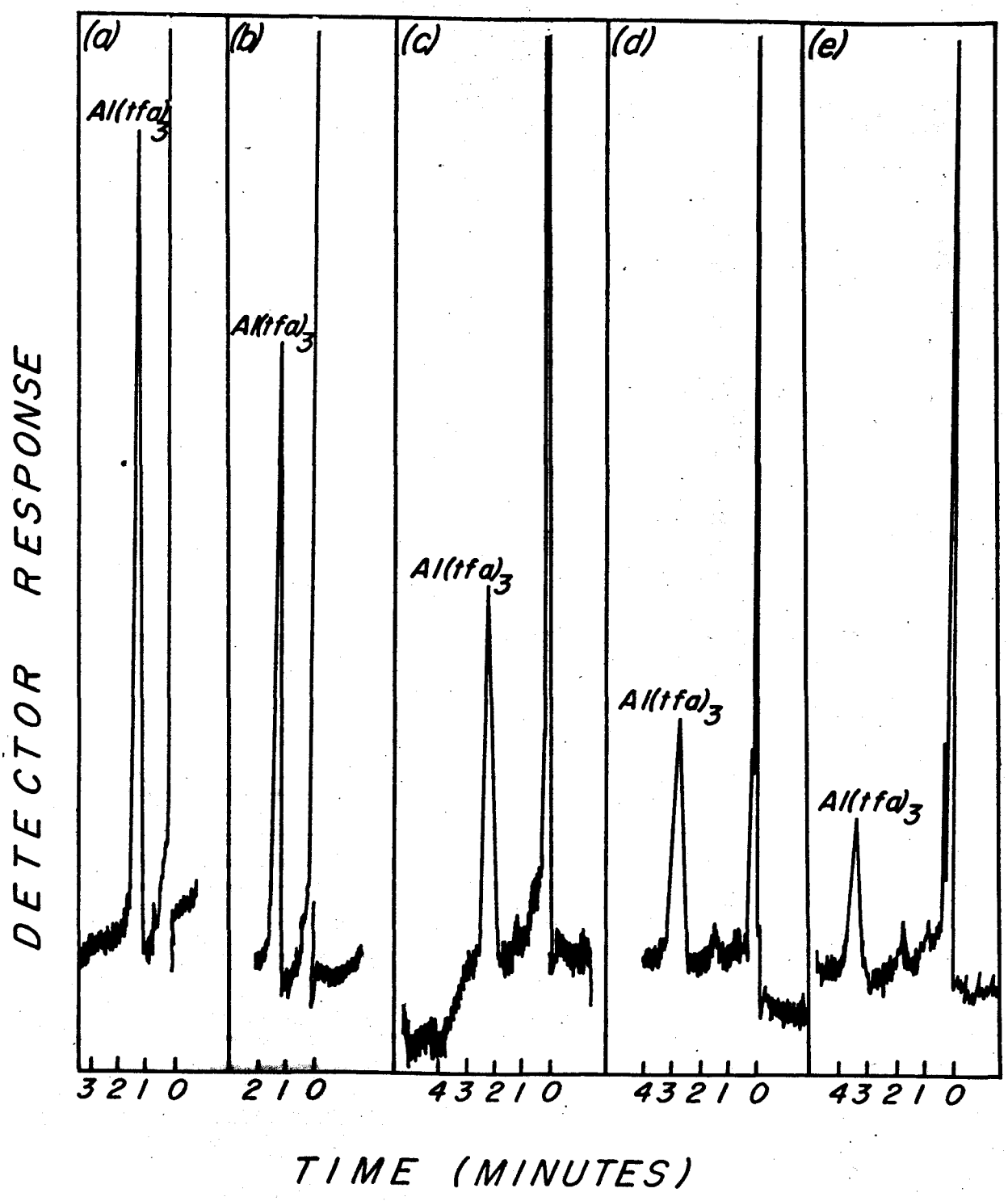


Fig. 9. Chromatograms of 1.1×10^{-9}g Al(tfa)$_3$ with different carrier gas flow rates. (a) 285 ml/min., (b) 229 ml/min., (c) 122 ml/min., (d) 91 ml/min., (e) 83 ml/min.. Carrier gas : prepurified nitrogen. Column : 5 ft.,6mm o.d. glass column, packed with 4.6% DC710 & 0.2% Carbowax 20M on 60/80 mesh Gas Chrom Z, Column temperature : 118 C. On column injection, injector temperature : 123 C. Detector temperature: 203 C. Applied voltage: 20 V. Chart speed : 0.25 in/min.. Sample size : 2 ul of 6×10^{-11}g Al as Al(tfa)$_3$ in nanograde toluene.

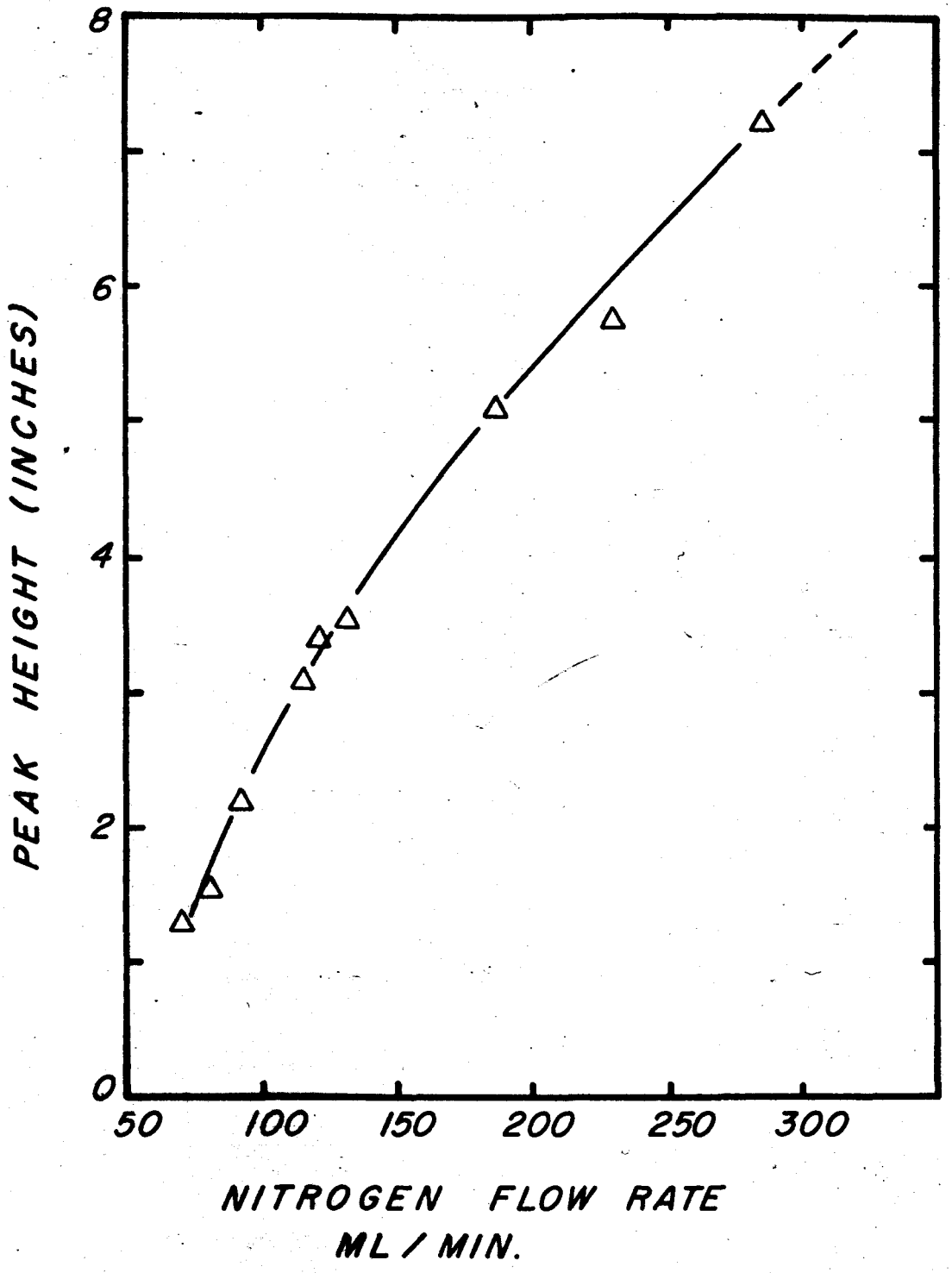


Fig.10. Change in electron capture detector response to 1.1×10^{-9}g $Al(tfa)_3$ with changes in carrier gas flow rate. Same column, instrument and column conditions as in Fig. 9.

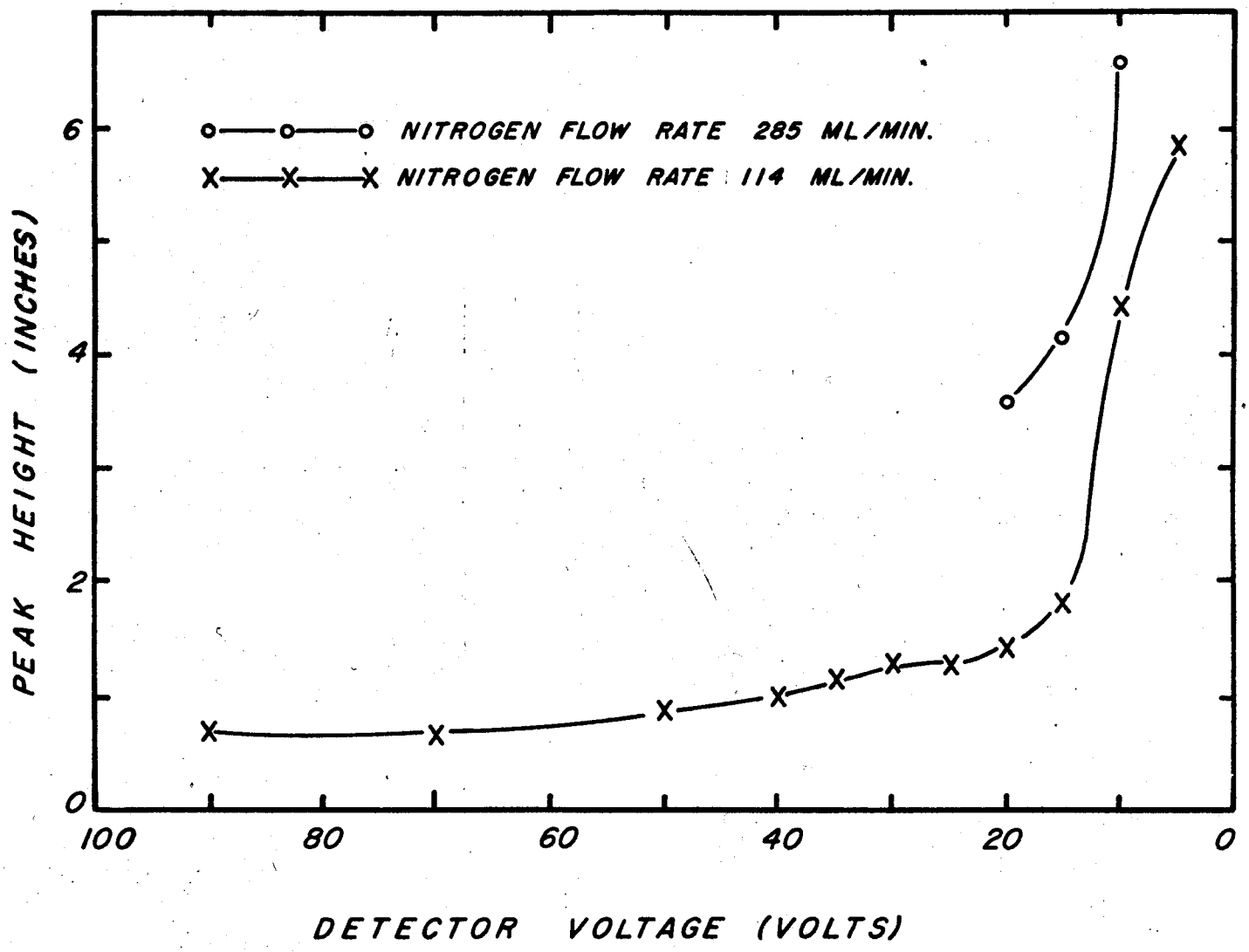


Fig. 11. Response of electron capture detector to 1.1×10^{-9} g $Al(tfa)_3$ at various conditions of flow rate and applied voltage. Same column, instrument and column conditions as in Fig. 12.

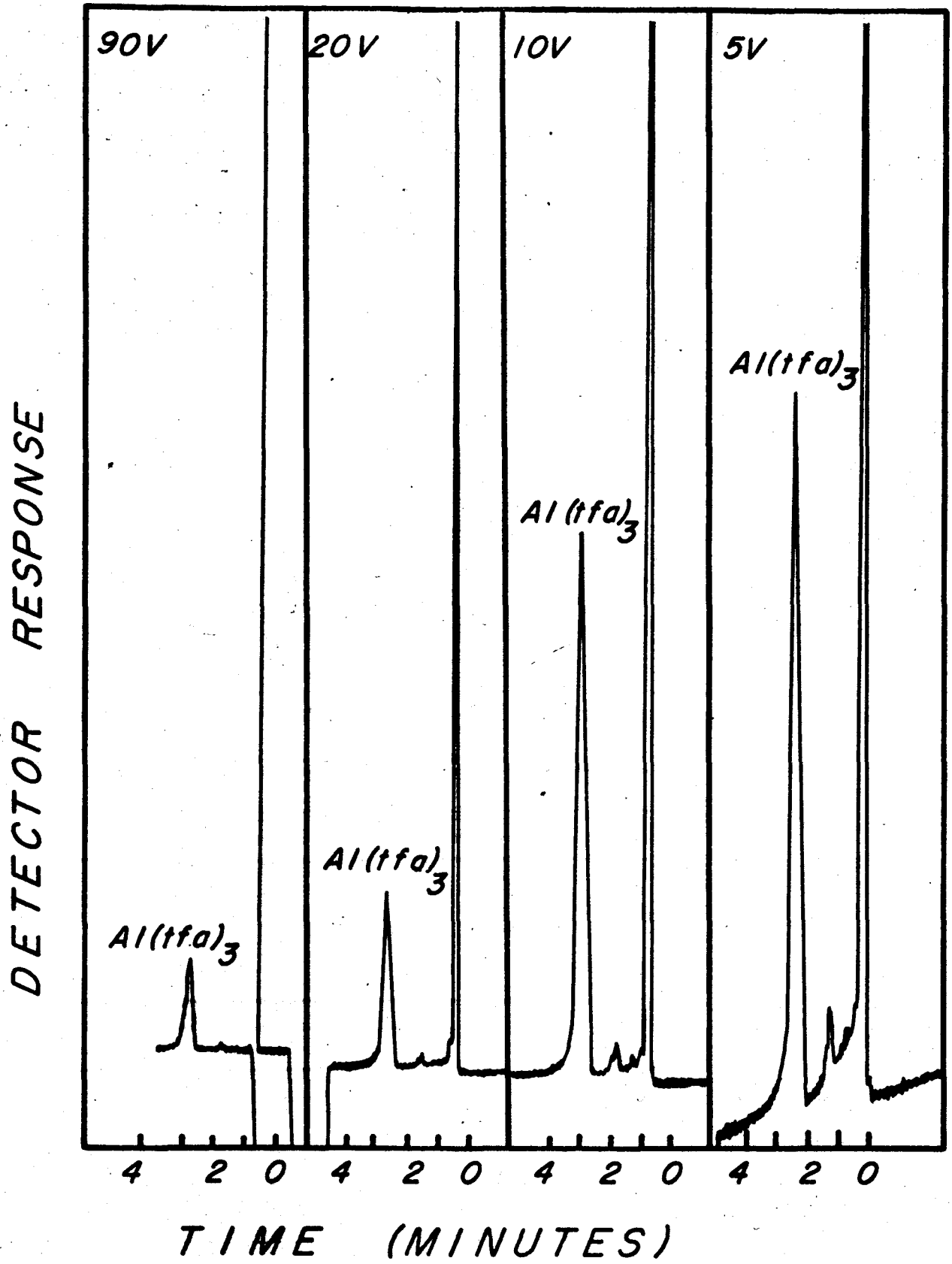


Fig. 12. Chromatograms of 1.1×10^{-9}g $Al(tfa)_3$ with different detector voltages. Same column, instrument and column conditions as in Fig. 9. Detector temperature: 205 C. Injector temperature: 122 C. Nitrogen flow rate : 114 ml/min.. Attenuation : 8.

Chromatograms

In-tfa: A very broad peak for the chelate was recorded at high concentrations (> 10^{-7}g), but no peak was observed when its concentration was lower than 10^{-8}g.

Fe-tfa: Same results as for In-tfa.

Cu-tfa: Same results as for In-tfa.

Al-tfa: The peaks for this chelate are good; the relocation time is short; and the sensitivity is excellent (Figs. 9, 10, and 14). The chromatogram for testing the extractability of Al from seawater is shown in Fig. 13a.

Metal ions present in natural seawater and lake water samples were converted into metal-tfa complexes and transferred to the organic phase by the solvent extraction methods described. An aliquot of the organic solution was injected into the glpc unit. The results are shown in Figs. 13b and 13d. No chelate peak except Al-tfa is observed. The Al-tfa of the samples is well separated from other peaks and the sensitivity for Al in the lake sample is excellent (attenuation 16). Chromatography for seawater and lake water samples was carried out at different column and different instrument conditions as shown in the footnotes of the various figures. The non-appearance of the other potential chelate peaks is probably due to the loss or dispersion of the chelates in the column as discussed above. A blank test was carried out along with the sample preparation; the value for this was somewhat high (Fig. 13c).

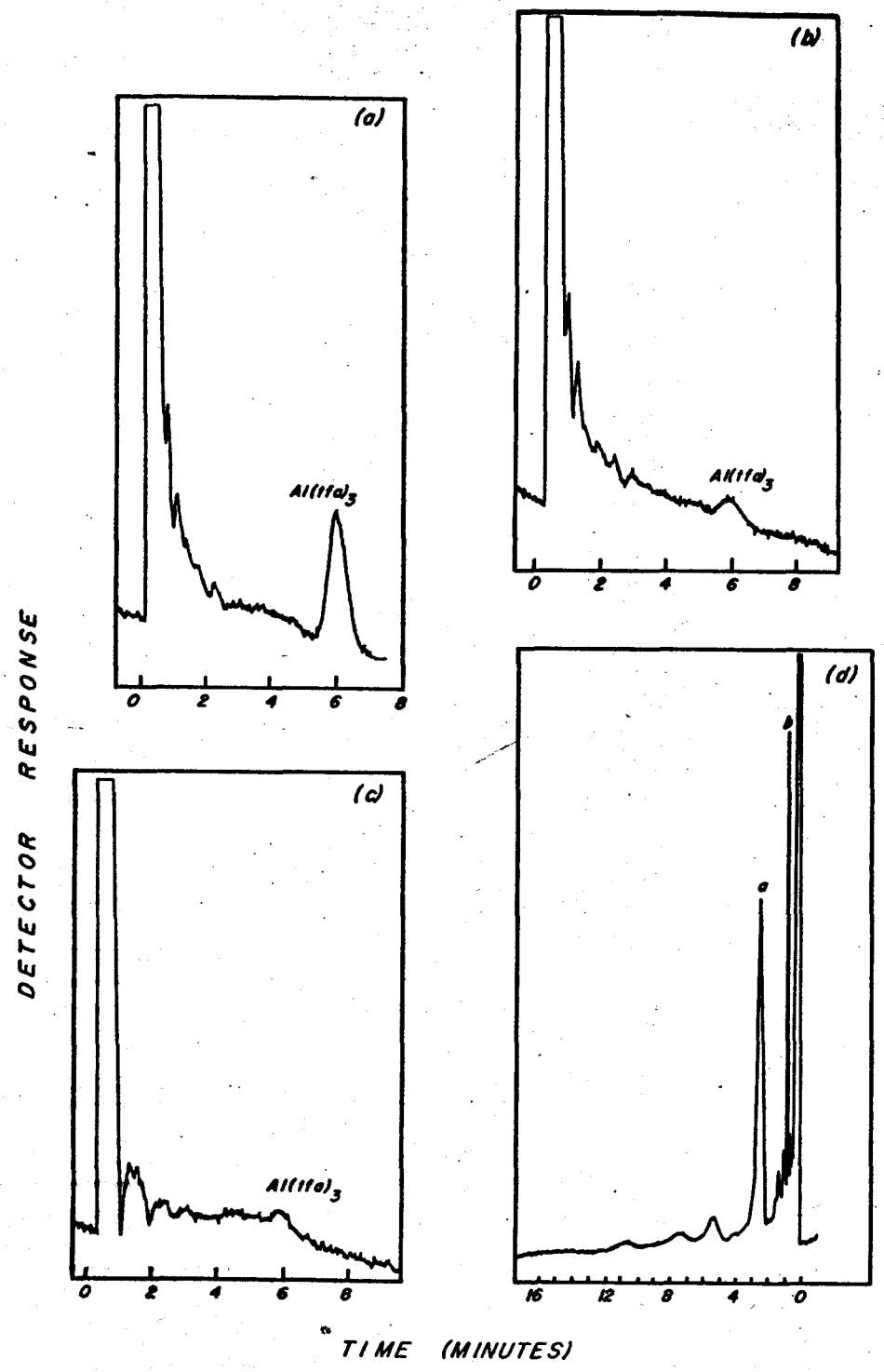


Fig. 13.

(a) Chromatogram of a sea water sample with the addition of 1 ppm Al. (b) Chromatogram of a sea water sample. (c) Blank. Nitrogen flow rate: 55ml/min.. Column : 5.08% silicone 30 & 0.34% carbowax 20 M on 60/80 mesh Gas Chrom Z,glass column. Column temperature : 119 C. Detector temperature : 205 C. Applied voltage : 20V. On column injection, injector temperature: 124 C. Chart speed : 0.5 in/min. (Sargent recorder).

(d) Chromatogram of a water sample of Smith lake,College,Alaska. Same column, instrument and column conditions as in Fig. 10. Attenuation : 16.
a. $Al(tfa)_3$ peak. b. unidentified.

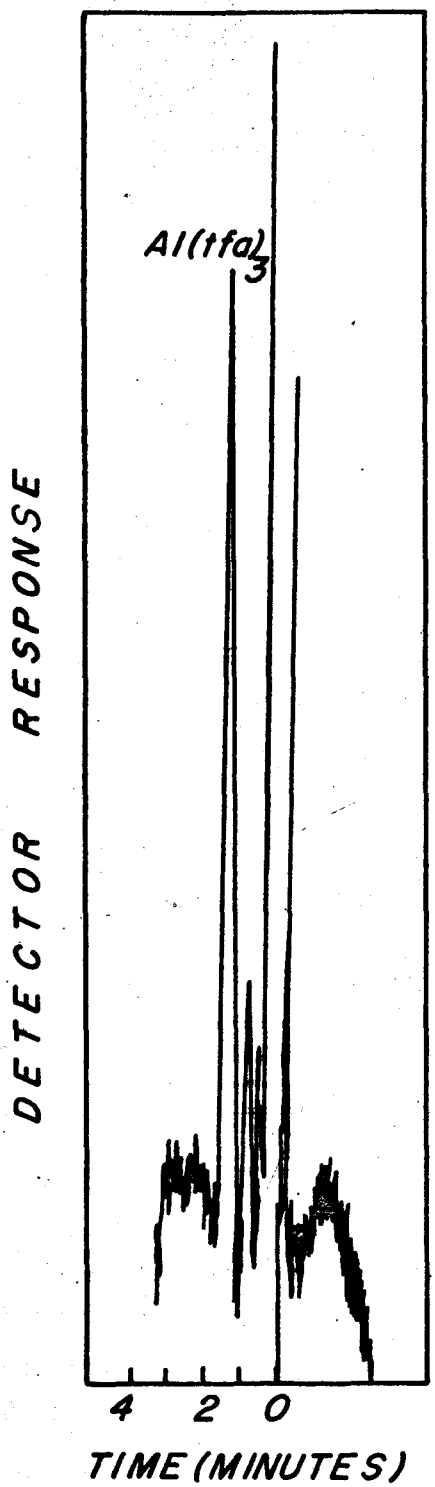


Fig. 14. Chromatogram of a standard solution of $Al(tfa)_3$ in toluene. Same column, instrument and column conditions as in Fig.8. Applied voltage: 5 V. Nitrogen flow rate: 285 ml/min.. Sample size : 2ul, 6.14×10^{-12}g of Al as $Al(tfa)_3$ in toluene.

DISCUSSION

A. Chelate Extraction Conditions

To obtain optimum extraction conditions for metal-tfa chelates from seawater, it is necessary to evaluate the parameters which govern the extraction efficiency. Factors which favor a high extraction of metal from the aqueous solution include:

1. The acid dissociation constant is relatively high and the solubility of the chelating agent in the aqueous solution is also fairly high. If the formula of the reagent, trifluoroacetylacetone, is written as HR, the ionization and distribution of HR in seawater can be described by the following equations (K data from Wakahayaski, et al., 1964):

$$\text{Ionization} \qquad HR \rightleftharpoons H^+ + R^- \qquad K_a = \frac{[H^+][R^-]}{[HR]} = 5\times10^{-7}$$

and the distribution of HR between seawater and toluene:

$$K_d = \frac{[HR]_o}{[HR]_w} = 0.57$$

As pointed out by Sillen (1967), equilibrium constants on an "ionic medium" scale are thermodynamically as well defined as those on the infinite dilution scale. Since seawater, ionic strength 0.7, has a constant major ion composition, the K_a value should be made on this "constant medium" activity scale. The K_a given above, calculated by Wakahayaski et al. (1964) is valid only for dilute solutions of ionic strength 0.1. However, no attempt has been made to correct the value for "seawater medium" scale, although most thermodynamical laws (e.g., Debye-Huckel), due to fundamental assumptions in the theory, fail at high ionic strength. But for our purposes, it suffices to mention that

the dissociation constant, K_a^*, in seawater medium would be greater than K_a, because of the salt effect.

ii. The initial pH of the aqueous solution directly affects the reaction. The chelating agent tfa is acidic, and the formation of a chelate is accompanied by the displacement of a proton. The time to reach equilibrium is largely limited by the rate of chelate formation, which, in turn, depends upon the concentration of tfa anion in the aqueous phase. The concentration of the anion is influenced by the pH of the aqueous solution. Thus:

Formation of anion	$HR \rightleftharpoons H^+ + R^-$	at low pH
	$HR \rightleftharpoons H^+ + R^-$	at high pH
Formation of chelate	$M^{+n} + nR^- \overset{K_f}{\rightleftharpoons} MR_n$	
Over-all reaction	$M^{+n} + nHR \rightleftharpoons MR_n + nH^+$	

The last equation shows how the concentration of hydrogen ions governs the direction of the reaction. At low pH, the reaction shifts to the left, and at high pH, to the right, i.e. favoring the chelate formation.

iii. Extraction time is a critical factor in solvent extraction. Effects within this system have been noted by Scribner et al. (1965).

iv. Of no less importance is the concentration of tfa. Because the quantities of the extractable elements in seawater are very small, minute amounts of tfa, about 10^{-4}M, would theoretically suffice for quantitative extraction of the elements of interest. The concentration of metal ions is also one of the factors controlling the extraction efficiency. However, this factor can be eliminated if the concentration of the chelating agent in the aqueous phase does not change during the extraction, regardless of the amount of metal being extracted. In addition, use of high concentrations of tfa will shorten equilibrium time, permit

the extraction to be carried out in more acidic solution than has been hitherto possible; and minimize absorption losses on the walls of the vessels (Ross and Sievers 1968).

v. Ions in seawater act as salting-out agents, electrolytes whose presence greatly enhances the extractability of chelates by decreasing the solubility of non-electrolytes. Another important aspect in salting-out is the binding of water molecules by cations. Water is presumably bound as a shell of oriented dipoles around the ions, thereby depleting water molecules for use as a solvent. If the metal ions of interest and the tfa anion are considered as definite though transient ion pairs, then they are brought together by electrostatic attraction. The association of the pairs will be greater the lower the dielectric constant of the solvent. One of the effects of the ions in seawater is to decrease the dielectric constant of seawater (Hasted, et al., 1948). Anions in seawater probably have the opposite effect on extraction.

It is interesting to compare the curves of Fe and In in Fig. 2 with the corresponding curves in Fig. 1 of Morie and Sweet (1966), and in Fig. 2 of Morie and Sweet (1965). Both curves for Fe and In (Fig. 2) determined in this study were less steep and were shifted toward higher pH values; one pH unit higher for Fe, two units for In. This phenomenon may be attributed to the presence of a high concentration of halogen ions in seawater despite the difference in ionic strength of the media, while the difference in degree of the metal hydrolysis in the two media is considered negligible. The halogen ions form more stable complexes than water molecules with these metal ions (other anions in seawater may be neglected when their relative concentrations are taken into consideration). Steinbach and Freiser (1954) have derived the following equation for the effects of complex formation on the chelate distribution between organic and aqueous phases:

$$D = \frac{(P_c - D)}{1+K_x(X^-)} \cdot \frac{(K_a^n (HR)_w^n K_f)}{(H^+)^n}$$

Where Pc is the partition coeffient of the chelates, K_x is the equilibrium constant of the equation: $M^{+n} + X^- \overset{K_x}{\rightleftharpoons} MX^{(n-1)}$, and (X^-) is the halogen ion concentration. This distribution equation shows that: (i) With increasing (X^-), the slope of the resulting extraction curve would be less steep; (ii) Since (X^-) in seawater samples remained constant as the pH was varied, the shape of the curve will not change, because the term $K_x(X^-)$ drops out, when D is differentiated with respect to (H^+). In this case, the curve will be translated without distortion toward higher pH values. These considerations should be able to explain the phenomena of the change of slope and the shift of curves of In and Fe in Fig. 2 with respect to those curves of Morie and Sweet (see Fig. 15).

Fe and In with a coordination number of 6 evidently form coordination-saturated chelates with tfa and are extracted excellently into toluene from seawater. Zn and Co (II), however, (coordination number 6) are extracted poorly by toluene, since they contain two molecules of water. Displacement of the water molecules with isobutylamine will explain the results obtained (Figs. 5 and 7). These results are also fully in accordance with the conclusion of Alimasin and Zolotov (1962).

Cobalt has two important oxidation states in aqueous chemistry; II and III. According to Kranskopt (1956) and Fukai (1968), the dominant form of Co in seawater is the +2 valence state, probably because of the high oxidation potential needed for the oxidation of Co(II) to Co(III) (Cotton and Wilkinson 1967) :

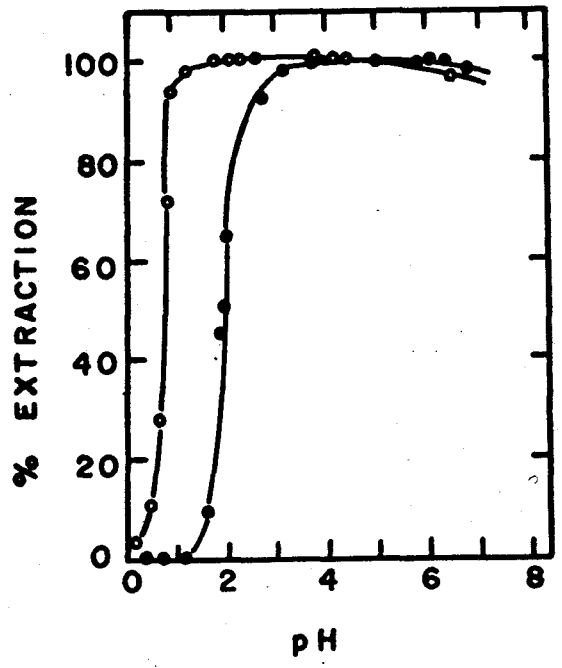


Fig. 15. Effect of pH on the extraction of In(III) and Fe(III) by 0.25M trifluoroacetylacetone in benzene. o , 8×10^{-3}M Fe; ● , 8×10^{-3} M In. from Morie and Sweet (1965), (1966).

$$[Co(H_2O)_6]^{3+} + e^- = [Co(H_2O)_6]^{2+} \quad E° = 1.84V$$

$Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$ are also far more stable than the corresponding Co(III) ions (Morrison and Freiser 1956). The oxidation state of cobalt in seawater is important here because Co(II) cannot be extracted into non-polar solvents as a trifluoroacetylacetone- chelate (Alimasin and Zolotov 1962). Adding isobutylamine to the system results in high extraction and, probably, the oxidation of Co(II). Co(II) is readily oxidized with oxidation agents and may be catalized with air, in the presence of complexing agents containing nitrogen donors (Cotton and Wilkinson 1967).

The equilibrium pH (the pH at which the rates of chelate dissociation and association are equal) was invariably lower than the initial pH value (Tables IV, VII). This was caused by the replacement of H^+ by metal ions extracted, and by the dissociation of the unchelated tfa.

Low extraction of all metal chelates occurs at low pH. This can be attributed to the decreased dissociation of tfa caused by the presence of a high concentration of H^+ in the aqueous solution, as discussed in (ii) above.

The electrolytes of seawater influence the extraction as can be demonstrated by comparing the data of this report with those of others. The equilibrium time for completed extraction of In-tfa reported by Morie and Sweet (1966) is more than one hour, while in this study (Fig. 3), total extraction of In is possible in less than five minutes. Zn and Co can be extracted with toluene-tfa (0.1M)-iba(0.4M) over a much wider pH range (Fig. 5) than that reported by Scribner and Kotechi (1965). Therefore, it seems safe to conclude that seawater, a medium of high ionic strength, is a better medium for solvent extraction of metal chelates

than a conventional one of ionic strength 0.1.

The extraction conditions for Al were not considered in this study. However, Genty et al. (1968), Morie and Sweet (1965, 1966), and Scribner et al. (1965) reported that Al was highly extracted from fresh water medium with tfa into benzene or chloroform at pH greater than 4, and Morie and Sweet (1956) also reported that the extractability of Al was as good as that of In over the pH range of 4-7, because (it was believed) that Al and In are of the same group on the Periodic table and should have similar chemical properties. And it has already mentioned above that seawater as an extraction medium is superior to a fresh water medium of ionic strength 0.1. So it is resonable to conclude that the extractability of Al from seawater should be as excellent as that of In with toluene- tfa (0.1M).

B. Gas Liquid Partition Chromatography

Column performance

For a general discussion of column performance, a simplified Van Deemter equation suffices:

$$HETP = A + B/_{\mu} + C \cdot \mu$$

where A is multipath effect or eddy diffusion constant; B is molecular diffusion; and C resistance to mass transfer (gas and liquid).

$$\mu = \frac{\text{length of column}}{\text{retention time of air}} = \text{average gas velocity}$$

HETP is the standard abbreviation for "height equivalent to a theoretical plate". A minimum HETP is that flow rate at which the column is operating most efficiently (μ optimum).

Molecular weight of a carrier gas affects a column's performance

through its effect on the parameter B of the equation above. The lighter and smaller the molecules of the carrier gas, the greater is the diffusion of the vapor within it. This effect is most obvious at slow flow rate. Hence nitrogen as a carrier gas is superior to other kinds of carrier gases of lower molecular weight.

In principle, if a wide column were perfectly evenly packed, it would be equivalent to many narrow columns in parallel and plate-height would be independent of diameter. But the major factor which causes wide columns to have greater plate-heights than narrow ones is that, with a larger column, the variations of carrier-gas velocity across the column is higher. A column should be packed as evenly as possible with a homogeneous size of support. A narrow column usually is superior to a wider one in column performance if sample size and column length are appropriate, but a narrow glass column is so fragile as to be easily broken during packing and changing of the column. This is why 4 mm i.d. (6 mm o.d.) columns have been used in this study.

Change of temperature affects performance principally through the change that it causes in the partition coefficient. The change in partition coefficient with temperature can be described by the following equation derived from Clausius-Clapeyron equation:

$$\frac{d\ln\beta}{dt} = \frac{1}{RT^2} \quad (-\Delta H_s + RT)$$

ΔH_s is the heat of evaporation of a dilute solute from a solution. As the temperature is reduced, the partition coefficient increases, and hence the value of C decreases, thus improving the performance. Low liquid loadings have the advantage of fast analysis and lower temperature operation; they reduce, however, the sample capacity and may require highly inactive solid supports. For maximum efficiency the column must be

operated at the optimum flow rate for which the analysis time is minimum and HETP is not materially affected.

The most serious chromatographic problem encountered during this study has been loss of chelates in the column. No peaks for In, Fe, and Cu-tfa chelates were given by concentrations lower than 10^{-8}g in any column except the one whose liquid was carbowax 20M. The loss of chelates makes the investigation of HETP impossible. The surface of the support used (Gas Chrom Z) is polar in nature and therefore tends to adsorb polar compounds. Under the operating temperature-range conditions used, the compounds are removed from the surface and eluted from the column. Thus the active sites on the support are exposed and tend to retard or adsorb completely a polar compound of the sample being analyzed. When a polar liquid phase was coated on the support, this compound would deactivate the active sites by strongly binding one end of the long chain molecule to the site. Non-polar liquid phases only poorly wet the polar surface. This is why the adsorption problem is less serious in the column of 13% carbowax 20M. The loss of chelates in the columns seems to be inversely proportional to the polarity of the liquid phases used.

Factors affecting electron capture performance

The success of the application of glpc to metal analysis may be attributed to the sensitivity and selectivity of the e.c. detector used. The fact is, that for a concentrations in the parts per billion range, it is almost impossible to achieve analysis by any other method without preconcentration.

The electron-capture detector (which measures a decrease in current), was designed for the analysis of substances having an affinity for free

electrons (Lovelock and Lipsky 1960). Two basic reactions of electron capture are:

$$AB + e^- \longrightarrow AB^- \quad \text{and} \quad AB + e^- \longrightarrow A^{\cdot} + B^-$$

Metal-tfa chelates do not undergo dissociation upon capturing an electron or electrons, since the energy of the C-F bond is sufficiently high compared with the electron affinity (Wentworth and Chen 1967).

The increased response of the e.c. detector with decreasing cell voltage has been well documented (Lovelock and Lipsky 1960; Landowne and Lipsky 1962), and the same result was obtained for the response of the e.c. detector to Al-tfa in this study (Figs. 10 and 11, Table XX) since electrons are more easily captured to form negative ions at low applied voltages. At low voltages, the electrons have comparatively smaller energies.

A direct current e.c. detector operated at low potential produces a current decrease if an electron absorbing vapor is present; however, it can also produce other responses by other mechanisms (Lovelock 1963). For example, the detector may act as a cross-section detector whether or not there is electron capture and, since vapor molecules are normally larger than carrier gas, will produce an increase in cell current due to the cross section effect in opposition to the electron capture effect. Since a high concentration of compound with no or low electron affinity would give such a false detector response (Lovelock 1963), the column used should be able to separate solvent or impurities from metal chelates. The columns employed in this study did not produce this problem.

The electron affinity of a given substance varies with the energy of the free electrons in much the same way as the absorption of light varies with the energy of the photons. The electron energy in the ion chamber of an e.c. detector has a mean value determined by the field strength and by the nature of the gas present. At a given field strength; the mean free electron energy is highest with the monatomic gases (since the collisions of electrons with the gases are in general highly elastic) and lowest with the polyatomic gases (Lovelock 1961). It is one of the reasons that nitrogen was chosen as the carrier gas instead of monatomic gas such as He.

CONCLUSIONS

A. Solvent Extraction

1. Indium and iron, and cobalt and zinc can be rapidly and completely extracted from seawater in a single extraction with an equal volume of toluene-tfa(0.1M), and toluene-tfa(0.1M)-isobutylamine(0.4M), respectively.

2. The deviation of the extraction curves of In and Fe from seawater, from a theoretical trivalent-metal extraction curve must be due to the presence of halogen ions.

3. Seawater is a better medium for this solvent extraction system than one of less ionic strength.

B. Gas Liquid Partition Chromatography

1. The response of the e.c. detector increases with decreasing applied potential, and with increasing flow rate, under the conditions used, up to 285 ml/min.

2. No detection of In, Fe, and Cu-tfa chelates was possible in concentrations $< 10^{-8}$g. This is believed that this was due to adsorption onto active sites of the solid supports or to the dispersion of the chelates in the column caused by the retardation of the active sites. This problem was found to be less serious when a polar stationary phase was used.

3. A concentration of Al as low as 6×10^{-12}g was detected.

4. The possibility of the application of electron-capture gas-liquid chromatography to the determination of Al in natural waters, especially in lake water, has proved feasible in this study. A concentration of 6.0 ppb Al in natural waters as the trifluoroacetylacetonate can be detected.

5. On-column injection alleviated sample thermal-decomposition problem.

FUTURE WORK

The inability of the method to determine In, Fe, and Cu in quantities less than 10^{-8} g suggests that a more inert (more non-polar) solid support should be sought. It seems surface leached sodium silicate glass beads may be a promising support (Filbert and Hair 1968). If a narrow teflon tube is used as column material, the inner wall of the tube should be coated with a layer of liquid phase to minimize the adsorption loss.

It is necessary to know the extractability of Al from seawater with solvent extraction and glpc, before quantitative work is carried on.

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APPENDIX

(TABLES)

TABLE I

Some physical properties of the trifluoroacetylacetone chelates (Moshier and Sievers 1965).

Element	Color	Isomer	Sublime Temp. °C	M.P.°C
Be	White	--	104	112
Al	Cream-white	trans	100	117, 121-2, 122*
Ga	White	trans	--	128.5-129.5
Sc	White	--	90-95	106-7
Cu	Blue-violet	--	90-95	189, 199.5*
Cr	Dark-violet	Cis	--	112-114
		trans	--	154.5-5.0
In	Ivory	trans	--	118-20, 123.5*
Rh	Yellow	Cis	--	148.5-9.0
		trans		189.5-190
Fe	Dark Red	trans	--	114, 114*
Mg	Dark green-brown	trans	--	113-114
Co	--	--	--	--
Zn	--	--	--	--

*Values obtained in this study.

TABLE II

Extraction procedure

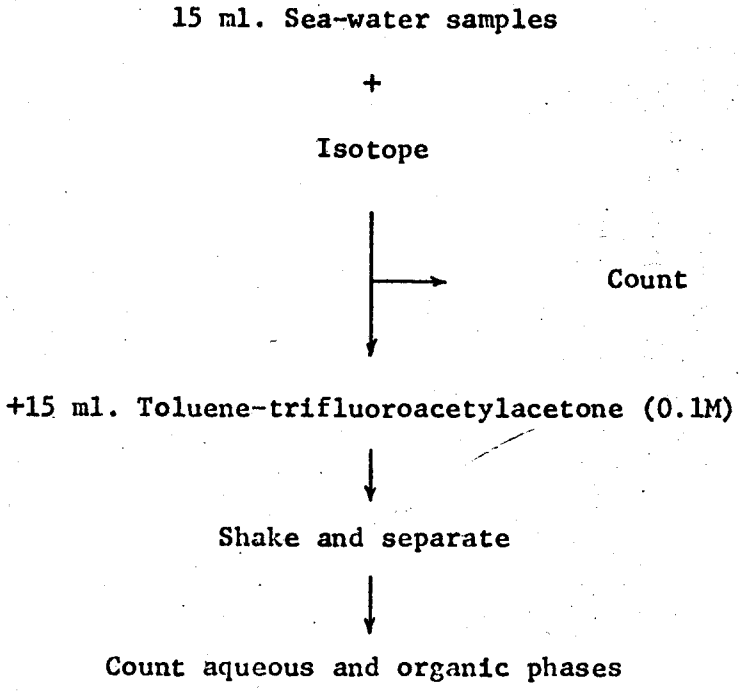

TABLE III

Properties of liquid phases

Liquid phase	Max temperature °C	Polarity	Solvent
Polyethylene glycol 600	125	polar	chloroform
Carbowax 20M	250	polar	chloroform
Apiezon L	300	non-polar	chloroform
Silicone D.C. 710	300	intermediate	chloroform
Silicone SE-30	300	non-polar	hot chloroform

TABLE IV

Effect of pH on extractability of indium

Isotope: In^{114m}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)

Time: 60 minutes

phase ratio 1:1

pH	Counts			Extraction (%)	Equil. pH
	Reference	Aqueous phase	Organic phase		
1.45	4320	4375	29	0.7	1.62
3.20	4470	4137	216	4.8	3.05
4.35	4126	2750	1428	34.6	3.33
5.51	4080	1287	2898	71	3.59
6.32	4460	121	4438	99.5	4.05
7.52	4282	61	4459	99.9	4.23
7.84	4371	44	4497	99.9	4.26
8.92	4439	25	4384	98.8	4.42
9.80	4511	44	4494	99.6	4.36
10.26	4381	24	4262	97.3	5.66

TABLE V

Effect of time on the extraction of indium

Isotope: In^{114m}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)

Initial pH = 7.84

phase ratio 1:1

Time (min)	Counts			Extraction (%)	Equil. pH
	Reference	Aqueous phase	Organic phase		
1	43347	2810	39524	93.5	4.98
5	43347	256	42959	99.4	4.49
10	43347	208	42431	99.5	4.38
30	43347	255	42910	99.4	4.41
60	43347	241	43337	99.4	4.42
120	43347	300	43479	99.3	4.40

TABLE VI

Efficiency of the extraction of indium as a function of water/organic volume ratio

Isotope: In^{114m}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)

Initial pH - 7.84

Time = one hour

Phase Ratio	Counts			Extraction (%)	Equil. pH
	Reference	Aqueous phase	Organic phase		
1	43347	241	43337	99.4	4.42
2	43347	491	83957	98.9	4.62
3	43347	377	126312	99.1	4.75
5	43347	1003	210196	97.7	4.90
10	43347	1786	435683	95.9	5.16
20	43347	4735	710748	89.1	5.44
40	43347	8095	1185906	81.3	5.90

TABLE VII

Effect of pH on extractability of iron

Isotope: Fe^{59}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)

Time: 10 minutes

phase ratio 1:1

pH	Counts			Extraction (%)	Equil. pH
	Reference	Aqueous phase	Organic phase		
1.45	83015	55659	26360	33	1.51
2.10	81876	14139	67748	82.7	2.07
3.20	81326	4124	76971	95	2.94
4.35	75440	894	75224	98.8	3.17
5.51	79064	2198	75108	97.3	3.42
6.32	80282	1208	80562	98.5	3.99
7.52	76581	2144	75004	97.2	3.95
7.84	76032	1289	75326	98.3	4.07
8.92	77621	1688	75422	97.8	4.39
9.80	78639	1450	77407	98.2	3.65
10.26	82039	1216	81019	99.7	5.79

TABLE VIIII

Effect of time on the extraction of iron

Isotope: Fe^{59}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)

Initial pH = 7.84

phase ratio 1:1

Time (min)	Counts			Extraction (%)	Equil. pH
	Reference	Aqueous phase	Organic phase		
1	32659	489	29390	92.4	4.72
5	32659	911	31208	97.2	4.30
10	44003	837	43486	98.1	4.15
30	32659	580	31674	98.2	4.26
60	32659	925	32034	98.4	4.28
120	32659	390	32282	98.8	4.26

TABLE IX

Efficiency of the extraction of iron as a function of water/organic volume ratio

Isotope: Fe^{59}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)

Initial pH: 7.84

Time: 10 minutes

phase ratio 1:1

Phase Ratio	Counts			Extraction (%)	Equil. pH
	Reference	Aqueous phase	Organic phase		
1	44003	837	43486	98.1	4.15
3	32659	1413	72430	95.7	4.56
5	32659	1577	129786	95.2	4.79
10	32659	1931	269639	94.1	5.06
20	32659	2603	519410	92.1	5.34
40	32659	3758	1050047	88.5	5.72

TABLE X

Effect of pH on extractability of zinc: (A)

Isotope: Zn^{65}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)

Time: 10 minutes

phase ratio 1:1

pH	Counts			Extraction (%)	Equil. pH
	Reference	Aqueous phase	Organic phase		
1.45	4901	4820	9	0.2	1.54
2.10	4971	4960	-8	0	2.13
3.20	5585	5627	-9	0	2.98
4.35	4563	4703	-17	0	3.31
5.51	4594	4678	4	0	3.53
6.32	4899	5300	0	0	4.02
7.52	5237	5024	-18	0	4.23
7.84	4992	5119	0	0	4.24
8.92	5391	5293	29	0.5	4.44
9.80	4897	4875	0	0	3.96
10.26	5968	5896	165	2.8	5.80

TABLE XI

Effect of magnesium on the extraction of zinc

Isotope: Zn^{65}

Reagents: toluene-trifluoroacetylacetone(0.1M)

Time: 10 minutes

phase ratio 1:1

	Sample No.	pH	Counts			Extraction (%)
			Reference	Aqueous phase	Organic phase	
a	1	4.05	23824	23558	20	0
	2	6.8	16750	15772	46	0
	3	10.85	22460	23531	142	0.6
	4	11.53	21997	20729	312	1.4
b	1	3.96	24504	24092	31	0
	2	5.8	16566	17272	35	0
	3	10.75	18226	23878	-6	0
	4	11.40	22357	23470	188	0.8
c	1	3.88	23960	23947	15	0
	2	6.8	16504	17321	225	1.4
	3	10.45	21507	23994	67	0
	4	10.97	23770	23424	23	0

Sample a's: D.D. H_2O

Sample b's: D.D. H_2O contains NaCl 10.6g/l.

Sample c's: D.D. H_2O contains NaCl 10.6g/l and $MgCl^2$ 1.3g/l.

TABLE XII

Effect of pH on the extraction of zinc (B)

Isotope: Zn^{65}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)-isobutylamine(0.4M)

Time: 10 minutes

phase ratio 1:1

pH	Counts			Extraction (%)	Equil. pH
	Reference	Aqueous phase	Organic phase		
1.45	1828	0	1831	100	9.33
2.10	1722	0	1922	100	9.92
3.20	1843	17	1794	99.1	10.07
4.35	1829	100	1661	94.5	10.1
5.51	1785	28	1692	98.4	10.3
6.32	1414	0	1628	100	10.1
7.52	1322	0	1328	100	10.06
7.84	1434	21	1472	98.4	10.1
8.92	1272	0	1429	100	10.1
9.8	1686	133	1524	92.1	10.9
10.26	1685	117	1514	93.05	10.1

TABLE XIII

Effect of time on the extraction of zinc

Isotope: Zn^{65}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)-isobutylamine(0.4M)

Initial pH: 7.84

phase ratio 1:1

Time (min)	Counts			Extraction (%)	Equil. pH
	Reference	Aqueous phase	Organic phase		
2	2411	9	2359	99.6	9.47
5	2411	26	2412	98.9	9.75
30	2411	24	2351	99.0	9.79
60	2411	16	2301	99.3	9.59
120	2411	13	2395	99.5	9.79
A	2411	32	2499	98.7	9.81

Sample A: The mixture of toluene-tfa-iba was prepared four hours before the extraction procedures were carried out. Results show the mixture is stable for at least four hours. Time was 10 minutes.

TABLE XIV

Efficiency of the extraction of zinc as a function of water/organic volume ratio

Isotope: Zn^{65}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)-isobutylamine(0.4M)

Initial pH: 7.84

Time: 10 minutes

phase ratio 1:1

Phase Ratio	Counts			Extraction (%)
	Reference	Aqueous phase	Organic phase	
2	7722	707	14916	96
3	7362	442	15353	94
5	7362	750	4418	90
10	7362	1403	3053	81
20	7362	2176	2469	71
50	7362	5965	--	19

TABLE XV

Effect of pH on the extraction of cobalt

Isotope: Co^{60}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)-isobutylamine(0.4M)

Time: 10 minutes

phase ratio 1:1

pH	Counts			Extraction (%)	Equil. pH
	Reference	Aqueous phase	Organic phase		
1.45	56986	156	57197	99.8	9.29
2.10	58448	539	58631	99.1	9.93
3.20	58126	812	56965	98.8	10.05
4.35	56603	491	57196	99.2	10.07
5.51	55797	838	54827	98.5	10.05
6.32	59128	471	59841	99.2	10.05
7.52	61000	588	61777	99.1	10.04
7.84	58708	823	58510	99.7	10.04
8.92	58113	738	58138	100	10.05
9.80	53309	526	52741	98.9	10.07
10.26	54305	909	54880	98.4	10.05

TABLE XVI

Effect of time on the extraction of cobalt

Isotope: Co^{60}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)-isobutylamine(0.4M)

Initial pH: 7.84

phase ratio 1:1

Time (min)	Counts			Extraction (%)	Equil. pH
	Reference	Aqueous phase	Organic phase		
1	16695	191	16137	98.9	9.87
5	16695	223	16202	98.7	9.87
30	16695	274	15951	98.6	9.90
60	16695	370	15648	97.8	9.91
120	16695	261	15758	98.5	9.88

TABLE XVII

Efficiency of the extraction of cobalt as a function of water/organic volume ratio

Isotope: Co^{60}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)-isobutylamine(0.4M)

Initial pH: 7.84

Time: 10 minutes

phase ratio 1:1

Phase Ratio	Counts			Extraction (%)	Equil. pH
	Reference	Aqueous phase	Organic phase		
1	58708	823	53510	99.66	10.04
2	16695	558	33153	96.7	9.75
5	16695	939	79282	94.4	9.66
10	16695	1763	95848	89.5	9.72
20	16695	5899	98576	64.7	9.48
45	16695	15290	13699	8.42	8.97

TABLE XVIII

Effect of the concentration of isobutylamine on the extraction of zinc

Isotope: Zn^{65}

Aqueous phase: Sea water

Reagents: toluene-trifluoroacetylacetone(0.1M)

Initial pH: 7.84

Time: 10 minutes

phase ratio 1:1

i.b.a. Added (ml)	Counts			Extraction (%)	Equil. pH
	Reference	Aqueous phase	Organic phase		
0.02	6527	6492	19	0.29	5.21
0.05	6527	4822	552	8.5	5.76
0.10	6527	--	3080	47.2	6.30
0.15	6527	2134	4627	70.9	7.19
0.20	6527	--	6245	95.7	9.75
0.30	6527	303	6459	98.96	10.21

The data of the first column represent the amount of isobutylamine added to 15ml toluene-tfa(0.1M) solution. Phase ratio is 1.

TABLE XIX

Change in detector response to $Al(tfa)_3$ with changes in nitrogen flow rate

Flow rate (ml/min.)	Peak height (inches)
71	1.3
83	1.55
91	2.25
115	3.1
122	3.4
133	3.56
186	5.15
229	5.76
285	7.25

The detector responded more strongly, but with unstable background signal, when flow rate was greater than 285 ml/min.

TABLE XX

Change in detector response to $Al(tfa)_3$ with changes in detector cell voltage

Nitrogen flow rate (ml/min.)	Cell voltage (V)	Peak height (inches)
114	90	0.7
	70	0.65
	50	0.88
	40	0.98
	35	1.14
	30	1.26
	25	1.25
	20	1.40
	15	1.82
	10	4.40
	5	5.80
285	20	3.60
	15	4.15
	10	6.58